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PATENT SPECIFICATION

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NO DRAWINGS

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COMPLETE SPECIFICATION

Dialdehyde Polysaccharide Derivatives

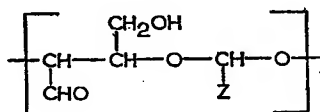
We, MILES LABORATORIES INC., a corporation organised and existing under the laws of the State of Indiana, United States of America, of 1127 Myrtle Street, Elkhart, Indiana, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to novel derivatives of dialdehyde polysaccharides and to processes for their preparation. More particularly, it relates to carboxyl, hydroxyperoxide and alkali metal peroxide derivatives of dialdehyde polysaccharides and to processes for their preparation.

Dialdehyde polysaccharides, such as dialdehyde corn starch, are well known in the art and are known to be useful to improve the wet strength of paper, for example. However, the water solubility and water dispersibility of dialdehyde polysaccharides are quite low and complicated procedures are necessary in order to get sufficient dialdehyde polysaccharide into dispersion so that the paper or the paper pulp can be properly treated with it. This is especially true when the dispersions are to be prepared in high concentrations containing as much as 20—30 weight percent solids.

It has now been found that when part of the aldehyde radical substituents of the dialdehyde polysaccharide are replaced with carboxyl, hydroxyperoxide or alkali metal peroxide radicals, the water solubility and dispersibility of the product are greatly increased. The derivatives of the present invention can also be isolated and collected as solids which can be employed as "building blocks" for additional chemical reactions.

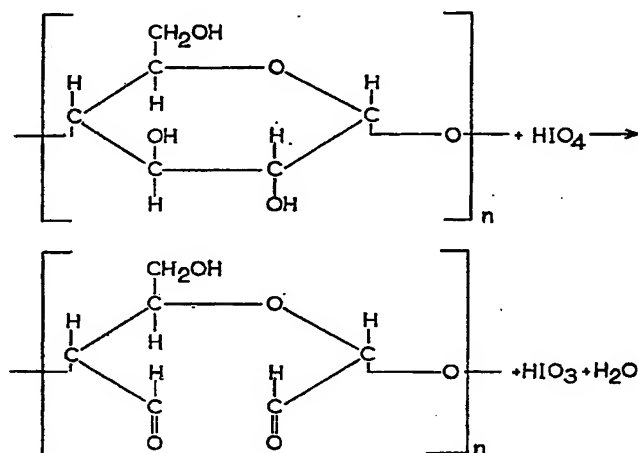
The novel compounds of the present invention include dialdehyde polysaccharide derivatives containing from about 0.5 to about 100 mole percent units represented by the formula:



wherein Z is a radical selected from the class consisting of —COOH, —CH—OOH, $\begin{array}{c} \text{OH} \\ | \\ \text{—CH—} \end{array}$

and —CH—OOM wherein M is an alkali metal. Preferably the compounds of the present invention are dialdehyde polysaccharide derivatives containing from about 90 to about 100 mole percent units of the above formula.

The novel compounds of the present invention are prepared from dialdehyde polysaccharides. Such materials are frequently referred to as periodate oxidized polysaccharides because of their preparation by the well known oxidation of polysaccharides with periodic acid. This preparation can be illustrated by the conversion of starch to dialdehyde starch or periodate oxidized starch using periodic acid in accordance with the following equation:

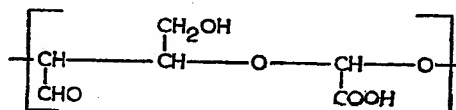


wherein n stands for the number of repeating structural units in the molecule, which may range from as few as about 20 to as many as several thousand.

The dialdehyde polysaccharides to be used as starting materials to prepare the novel compounds of the present invention may be the dialdehyde derivative of any polysaccharide, such as corn, wheat, rice, tapioca or potato starches, amyloses, amylopectins, celluloses, gums, dextrans, algin, inulins and the like. Of these polysaccharides, the dialdehyde derivatives of starch known generically as dialdehyde starch are the best known and most widely used. However, where it is desired to have derivatives of other polysaccharides, these may be used as well. The dialdehyde polysaccharides useful in the present invention can contain from about 0.5 to about 100 mole percent dialdehyde saccharide units. In general, it is preferred to use dialdehyde polysaccharides which are about from 90% to 100% oxidized; i.e., those wherein 90 to 100 of each 100 of the original anhydroglucose units have been converted to dialdehyde units such as by periodate oxidation as above described.

Alkali metals represented by M in the above formula are illustrated by sodium, potassium, lithium, rubidium and cesium.

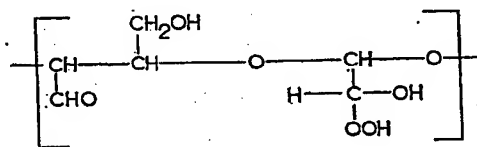
In accordance with the present invention, a dialdehyde polysaccharide containing from about 0.5 to about 100 mole percent dialdehyde saccharide units in the form of a slurry with water, water-miscible organic liquid, or mixture of water and water-miscible organic liquid is reacted with hydrogen peroxide at a reaction temperature of from about 20° C. to about 60° C. The starting material slurry has a weight ratio of dialdehyde polysaccharide to liquid of from about 1/4 to about 1/20. Preferably the slurry has a weight ratio from about 1/6 to about 1/10. Water is the preferred liquid in the slurry. Water-miscible organic liquid, such as methanol, ethanol, isopropanol, acetone, methylethylketone and the like can also be used alone or in admixture with water. When the desired product contains units represented by the formula:



the reaction temperature is preferably from about 40° C. to about 60° C. An acidic catalyst, such as sulfuric acid, phosphoric acid, formic acid, acetic acid, propionic acid and the like, is preferably used to form the carboxy aldehyde derivatives. The acid catalyst is present in the reaction mixture in an amount from about 0.5 to about 5.0 weight percent acid based on anhydrous weight of dialdehyde polysaccharide being employed. Preferably, the acid catalyst is present in an amount from about 1 to about 2 weight percent. It is further preferred to add the acidic catalyst to the dialdehyde polysaccharide slurry in an aqueous dilute form containing from about 5 to about 10 weight percent acid. The hydrogen peroxide is added in the form of an aqueous

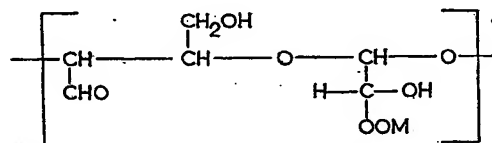
solution containing from about 30 to about 50 weight percent hydrogen peroxide. The reaction time is dependent principally upon the reaction temperature and whether an acidic catalyst is present. At temperatures below about 40° C., and without a catalyst, reaction times as long as 6 hours are needed. At 40° C. and with no catalyst, the reaction time is about 3 hours. At 40° C. and with about 1 weight percent acid catalyst the reaction time is about 1 hour. The amount of carboxyl substitution in the desired product can be controlled by the amount of hydrogen peroxide added to the reaction mixture. For example, if it is desired to convert an aldehyde radical to a carboxyl radical in each dialdehyde saccharide unit of the starting material, then at least 100 weight percent excess hydrogen peroxide should be used based on theoretical amount required to react with one aldehyde group of each unit. If it is desired to convert an aldehyde radical to a carboxyl radical in only about half of the dialdehyde saccharide units, then about 50—100 weight percent theoretical excess hydrogen peroxide may be used. Likewise, if it is desired to convert an aldehyde radical to a carboxyl group in about 25 percent of the dialdehyde saccharide units, then about 5—50 weight percent excess may be used. In other words, the lesser the amount of conversion of aldehyde group to carboxyl group through oxidation, the lesser the theoretical excess amount of hydrogen peroxide required. It is noted that only one aldehyde radical in a dialdehyde saccharide unit is oxidized by the hydrogen peroxide and this aldehyde radical is attached to the glyoxal moiety of the dialdehyde saccharide structure. The glyoxal moiety is so-called because when a dialdehyde polysaccharide is hydrolyzed, the polymer units cleave to form fractions of erythrose and glyoxal. The desired carboxyl-aldehyde derivative of dialdehyde polysaccharide is recovered by filtration to collect the solids followed by a water wash to remove excess hydrogen peroxide. Yields of desired product have been obtained which are about 95—100% of theory. This product is readily dispersible in water and is useful in improving the wet strength of paper. These compounds are also useful as insolubilization agents for polypeptides, polyvinyl alcohols, polyacrylamides, polymeric amines and the like.

When the desired product contains units represented by the formula:



the reaction temperature is preferably from about 20° C. to about 40° C. Temperatures of about 20—60° C. can be generally used. The theoretical amount of hydrogen peroxide is employed; i.e., about one mole of hydrogen peroxide for each mole of dialdehyde derivatives to be reacted and an excess of about 100—200 weight percent is preferably employed. The hydroxy peroxide product is recovered by filtration. Substantially anhydrous conditions are employed to prevent hydrolysis of the desired product. Such compounds are completely soluble in room temperature water and are stable at normal room temperature but when heated to temperatures of at least 40—50° C. they decompose with a strong exothermic reaction releasing large quantities of carbon dioxide gas and formic acid. These compounds thus have utility as blowing agents in polymer systems and in the formation of cellular products having insulating properties.

When the desired product contains units represented by the formula:



wherein M is an alkali metal, the hydroxy peroxide product is first prepared as described above and the product is neutralized with an alkali metal hydroxide or alkali metal alcoholate, for example. Theoretical quantities of reactants are generally

employed. This alkali metal peroxide derivative is readily soluble in water and is useful in improving the wet strength of paper. These alkali metal derivatives are also useful as insolubilization agents for polypeptides, polyvinyl alcohols, polyacrylamides, polymeric amines and the like.

When the novel compounds of the present invention are used to improve the wet strength of paper they are preferably used in combination with a cationizing agent or retention aid to assist in coupling the dialdehyde polysaccharide derivative to the paper. These cationizing agents are the well known cationic starches, polymeric amines and polyamides. The cationizing agent can be added first to a slurry of paper pulp followed by addition of the novel compounds of the present invention or the cationizing agent and present novel compounds can be mixed together and this mixture applied to the paper pulp slurry. Water soluble compounds of zirconium, such as zirconium oxychloride, can also be used as cationizing agents.

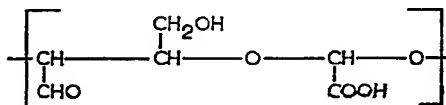
The following examples serve to illustrate, but not to limit, the practice of this invention.

EXAMPLE 1.

To a 5-liter, three-necked flask, equipped with thermometer and stirrer, were charged the following materials:

500 g. dialdehyde corn starch
(this contained 8 weight percent moisture and 95.7 weight percent of the anhydrous starch was oxidized starch in the form of dialdehyde starch).
3000 g. distilled water.
50 g. of 10 weight percent aqueous sulfuric acid.

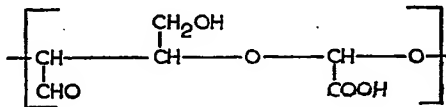
The above materials were mixed and the resulting slurry was stirred and heated at 40—45° C. To this heated slurry were added 93.6 g. (0.964 moles) of a 35 weight percent aqueous solution of hydrogen peroxide. The temperature was maintained at 40° C. for 1 hour and 15 min. The slurry was then filtered, the filter cake reslurried in 1000 ml. distilled water, filtered and washed with acetone. The product material was dried in a vacuum oven at 40° C. for 48 hours resulting in a yield of 522 g. The product contained 11.6 weight percent moisture (determined by Karl Fischer reagent) and also contained 24.9 mole percent units having the formula:



This latter figure was corrected for moisture and unoxidized starch. The hydrogen peroxide supplied was 41% in excess of the theoretical amount required to produce the product.

EXAMPLE 2.

A slurry consisting of 500 g. of the dialdehyde corn starch described in Example 1, 1800 g. distilled water, and 93.6 g. (0.83 mole) of 30 weight percent aqueous hydrogen peroxide was stirred and heated at 42—44° C. for 3 hours. The slurry was then filtered, washed with water several times, followed by an acetone wash, and then dried for two days at room temperature to yield 625 g. of a product containing 20.8 weight percent moisture (determined by Karl Fischer reagent) and also containing 25.3 mole percent (corrected for moisture and unoxidized starch) of units having the formula:

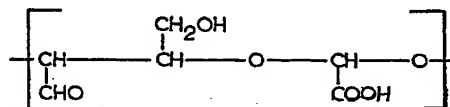


The hydrogen peroxide supplied was about 19 percent in excess of the theoretical amount required to produce the product.

The following example describes reaction using alcohol-water system and formic acid as the catalyst.

EXAMPLE 3.

A slurry consisting of 100 g. of the dialdehyde corn starch described in Example 1, 400 g. distilled water, 300 g. isopropanol, 3 g. of 90 weight percent aqueous formic acid and 92.8 g. (1.36 mole) of 50 weight percent aqueous hydrogen peroxide was stirred and heated at 40—45° C. for two hours. The mixture was then filtered, washed with water and then with acetone. The solid material was dried at room temperature for 24 hours and the yield was 102 g. The product contained 7.9 weight percent moisture (determined by Karl Fischer reagent) and it also contained 72.5 mole percent (corrected for moisture and unoxidized starch) of units having the formula:

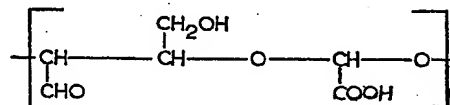


The hydrogen peroxide supplied was about 250 percent in excess of the theoretical amount required to produce the product.

The following two examples illustrate use of different starches to prepare derivatives of the present invention.

EXAMPLE 4.

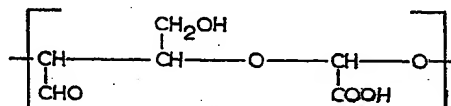
A slurry of 150 g. dialdehyde potato starch (this contained 11.1 weight percent moisture and 93.1 weight percent of the anhydrous starch was oxidized starch in the form of dialdehyde starch), 500 g. isopropanol, 100 g. distilled water, 1 g. of 10 weight percent aqueous sulfuric acid and 174 g. (2.56 mole) of 50 weight percent aqueous hydrogen peroxide was stirred and heated at 40° C. for 4 hours and then filtered, washed with water and then with acetone. The final product was dried at room temperature for 24 hours to yield 158 g. of material containing 7.35 weight percent moisture (determined by Karl Fischer reagent) and also containing 83.2 mole percent (corrected for moisture and unoxidized starch) of units having the formula:



The hydrogen peroxide supplied was about 294 percent in excess of the theoretical amount required to produce the product.

EXAMPLE 5.

A slurry of 100 g. dialdehyde amylose (this contained 16.5 weight percent moisture and 93.5 weight percent of the anhydrous amylose was oxidized amylose in the form of dialdehyde amylose), 200 g. isopropanol, 200 g. distilled water, 1 g. of 90 weight percent aqueous phosphoric acid and 102 g. (1.5 mole) of 50 weight percent aqueous hydrogen peroxide was stirred and heated at 47—51° C. for 3 hours and then filtered, washed with water and then with acetone. The final product was dried at room temperature for 24 hours to yield 99 g. of material. This product contained 7.7 weight percent moisture (determined by Karl Fischer reagent) and 85.1 mole percent (corrected for moisture and unoxidized starch) of units having the formula:



The hydrogen peroxide supplied was about 262 percent in excess of the theoretical amount required to produce the product.

The following example describes preparation of a hydroxyperoxide derivative of dialdehyde starch.

EXAMPLE 6.

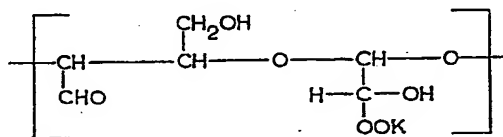
One hundred (100) grams of dialdehyde corn starch (containing 1.4 weight percent moisture and 94.4 weight percent of the anhydrous starch was dialdehyde starch)

was slurried in 400 ml. of isopropanol containing 3 ml. of 85 weight percent phosphoric acid and 40.8 g. (0.6 mole) of an aqueous 50 weight percent hydrogen peroxide solution. The slurry was heated for one hour at 50° C. It was then cooled, filtered, and the filtrate washed with 200 ml. of isopropanol. This product was a hydroxyperoxide derivative of dialdehyde starch. Sixteen (16) grams of the total mother liquor (above filtrate) of 515 g. was diluted with water and acidified with 12 ml. of a 20 weight percent sulfuric acid solution. It was titrated with a 1-Normal KMnO_4 solution to determine the unreacted amount of hydrogen peroxide. The consumption of 24.6 ml. of KMnO_4 correspond to 2.61 weight percent (0.395 moles) of hydrogen peroxide in the mother liquor. The amount of hydrogen peroxide consumed by the dialdehyde starch was thus 0.205 moles. This indicated that about a third of the dialdehyde starch units each contained a hydroxyperoxide group. The hydrogen peroxide supplied was about 184 percent in excess of the theoretical amount required to produce the product.

The following example describes preparation of an alkali metal peroxide derivative of dialdehyde starch.

EXAMPLE 7.

A slurry of 100 g. of the dialdehyde corn starch described in Example 1, 500 ml. isopropanol, and 46.4 g. (0.68 moles) of 50 weight percent aqueous hydrogen peroxide was stirred and heated from 28° C. to 38° C. The slurry was stirred for two more hours and heated from 36° C. to 38° C. To this slurry were added 50 ml. of 0.54 Molar aqueous potassium hydroxide solution (1.275 g. KOH). The product was filtered, washed with distilled water and dried. The residual alcoholic mother liquor was analyzed for KOH and none was found indicating complete reaction of the KOH with the oxidized dialdehyde starch. The final product thus contained units of the formula:



The following examples describe utility for the products of the present invention.

EXAMPLE 8.

Bleached sulfite pulp was beaten in a laboratory beater to a Canadian Standard Freeness of 450 ml. The pulp was diluted to a consistency of 1 weight percent based on oven dry pulp and mixed with 2 weight percent alum (based on oven dry pulp) to lower the pH. Handsheets of this pulp were prepared on standard equipment, such as a Noble and Wood Handsheet Machine. The remaining portion of the above pulp was then mixed with 0.2 weight percent (based on oven dry pulp) of a polycondensation product of adipic acid with diethylenetriamine partially crosslinked with epichlorohydrin. This cationic polyamide was added to aid in retaining a subsequently added polysaccharide derivative in the pulp. The cationic material was mixed with the pulp for 5 min. after which the pH of the treated pulp slurry was adjusted to 4.5 by addition of 1—2 weight percent sulfuric acid (based on oven-dry pulp weight). A portion of the pulp containing the cationic polyamide was used to make some handsheets. The remaining portion of the pulp was divided into separate portions each sufficient to make handsheets of the same basis weight as the handsheets previously prepared from the untreated pulp and pulp containing cationic polyamide. Each portion of this remaining pulp was mixed for 15 seconds with 0.5 weight percent (based on oven-dry pulp) of a carboxyl-aldehyde polysaccharide dispersion after which time the treated pulp was transferred to a sheet mold and a handsheet formed. The dispersion employed was previously prepared by mixing 30 g. of the carboxyl-aldehyde polysaccharide product of Example 1 with 1000 ml. distilled water and heating such mixture to 83—85° C. for 20 minutes to completely disperse the carboxyl-aldehyde polysaccharide material. The dispersion was then cooled to room temperature and diluted with distilled water to a concentration of 1 weight percent solids. The handsheets prepared above were conditioned according to TAPPI Standard T402-m-49. The handsheets were then soaked in water at room temperature for 5 min. and the wet tensile strength of each sheet was measured. The tensile strength data is shown below.

	Paper	Wet Tensile Strength (lbs. force/in. width)	
	No additive	0.89	
	Cationic Polyamide Additive	0.70	
5	Cationic Polyamide-Polysaccharide Derivative Additives	2.35	5

It can be seen from the above data that the presence of a carboxyl-aldehyde polysaccharide derivative of the present invention greatly improves the wet strength of paper.

- 10 Paper obtained from pulp treated in a similar manner with cationic polyamides and hydroxyperoxide or alkali metal peroxide derivatives of dialdehyde polysaccharides also had comparable improvements in wet tensile strength. 10

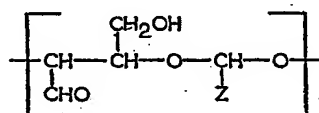
EXAMPLE 9.

- 15 A 0.2 in. thick layer of hydroxyperoxide derivative of dialdehyde starch prepared as in Example 6 was placed on a metal sheet and heated to about 40—50° C. A strong exothermic reaction commenced releasing large quantities of gas and expanding the material to a height of about 3 in. The rigid cellular material thus formed can be used as a thermal insulator. 15

- 20 In summation, the present invention relates to novel carboxyaldehyde, hydroxyperoxide aldehyde, and alkali metal peroxide aldehyde derivatives of dialdehyde polysaccharides. It also relates to a novel process of preparing such compounds employing controlled conditions for hydrogen peroxide oxidation of dialdehyde polysaccharides. 20

WHAT WE CLAIM IS:—

- 25 1. Dialdehyde polysaccharide derivatives containing from 0.5 to 100 mole percent of units represented by the formula: 25



wherein Z is a —COOH , —CH—OOH , or —CH—OOM radical and M is an alkali metal.

- 30 2. Dialdehyde polysaccharide derivatives as claimed in claim 1 substantially as described with reference to any of the Examples. 30

- 35 3. A process for preparing oxidised derivatives of dialdehyde polysaccharides according to claim 1 which comprises forming a slurry of dialdehyde polysaccharide containing from 0.5 to 100 mole percent of dialdehyde saccharide units in water, water-miscible organic liquids, or mixtures of water and water-miscible organic liquids, which slurry contains a weight ratio of dialdehyde polysaccharide to liquid of from 1/4 to 1/20, and contacting the slurry with hydrogen peroxide at a reaction temperature of from 20° C. to 60° C. 35

- 40 4. A process as claimed in claim 3 wherein an acidic catalyst is present in the reaction mixture in an amount from 0.5 to 5 weight percent based on anhydrous weight of dialdehyde polysaccharide. 40

5. A process as claimed in claim 3 for preparing carboxyaldehyde derivatives of dialdehyde polysaccharides wherein the slurry is contacted with hydrogen peroxide at a reaction temperature of from 40° C. to 60° C. 45

- 45 6. A process as claimed in claim 5 wherein an acidic catalyst is present in the reaction mixture in an amount from 0.5 to 5 weight percent based on anhydrous weight of dialdehyde polysaccharide. 45

- 50 7. A process as claimed in claim 5 or 6 which comprises forming a slurry of the dialdehyde polysaccharide containing from 90 to 100 mole percent dialdehyde saccharide units in water, water-miscible organic liquids, or mixtures of water and water-miscible organic liquids, which slurry contains a weight ratio of dialdehyde polysaccharide to liquid of from 1/6 to 1/10, adding acidic catalyst to the slurry in an amount from 1 to 2 weight percent based on anhydrous weight of dialdehyde poly- 50

saccharide, and contacting said acidic slurry with hydrogen peroxide at a reaction temperature of from 40° C. to 60° C.

- 5: 8. A process as claimed in claim 3 for preparing hydroxyperoxide aldehyde derivatives of dialdehyde polysaccharides wherein the slurry is contacted with hydrogen peroxide at a reaction temperature of from 20° C. to 40° C. 5

9. A process as claimed in claim 8 wherein the slurry contains from 90 to 100 mole percent dialdehyde saccharide units in a water-miscible organic liquid, and the slurry contains a weight ratio of dialdehyde polysaccharide to liquid of from 1/6 to 1/10.

- 10 10. A process for preparing alkali metal peroxide aldehyde derivatives of dialdehyde polysaccharides which comprises preparing a hydroxyperoxide aldehyde derivative in the process claimed in claim 8 or 9 and reacting the derivative with an alkali metal hydroxide or alkali metal alcoholate. 10

- 15 11. A process as claimed in claim 3 to 10 substantially as described with reference to any of the Examples. 15

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